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(54) Title: PROCESS FOR PURIFYING PENTAFLUOROETHANE, PROCESS FOR PRODUCING THE SAME, AND USE THEREOF

(57) Abstract: ABSTRACT A process comprising bringing crude pentafluoroethane containing at least one compound selected from the group consisting of hydrofluorocarbons containing one carbon atom, hydrochlorofluorocarbons containing one carbon atom and hydrochlorocarbons containing one carbon atom, into contact with an adsorbent comprising a zeolite having an average pore size of 3 to 6 Å and a silica/aluminum ratio of 2.0 or less and/or a carbonaceous adsorbent having an average pore size of 3.5 to 6 Å, to reduce the content of the compound. The purified gas can be used as a low temperature refrigerant or an etching gas.

DESCRIPTION

Process for Purifying Pentafluoroethane, Process
for Producing the Same, and Use Thereof

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Cross-Reference to Related Application

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of the Provisional Application 60/394,267 filed July 9, 2002, pursuant to 35 U.S.C. §111(b).

10 Technical Field

The present invention relates to a purification process, a production process and uses of pentafluoroethane.

15 Background Art

Pentafluoroethane (CF_3CHF_2) is used, as examples, as a low temperature refrigerant or an etching gas and is also used as a starting material for the production of hexafluoroethane (CF_3CF_3).

20 For the production of pentafluoroethane, the following methods have heretofore been known, as examples,

(1) a method of fluorinating tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$) or a fluoride thereof with hydrogen fluoride (see, Japanese Unexamined Patent Publication No. 8-268932 (JP-A-8-268932)),

25 (2) a method of reducing and hydrogenating chloropentafluoroethane (CF_3CClF_2) (see, Japanese Patent No. 2540409), and

30 (3) a method of reacting a fluorine gas with a halogen-containing ethylene (see, Japanese Unexamined Patent Publication No. 1-38034 (JP-A-1-38034)).

The pentafluoroethanes produced by these methods contain various impurities such as hydrochlorocarbons (HCC), chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons

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(54) Title: PROCESS FOR PURIFYING PENTAFLUOROETHANE, PROCESS FOR PRODUCING THE SAME, AND USE THEREOF

(57) Abstract: ABSTRACT A process comprising bringing crude pentafluoroethane containing at least one compound selected from the group consisting of hydrofluorocarbons containing one carbon atom, hydrochlorofluorocarbons containing one carbon atom and hydrochlorocarbons containing one carbon atom, into contact with an adsorbent comprising a zeolite having an average pore size of 3 to 6 Å and a silica/aluminum ratio of 2.0 or less and/or a carbonaceous adsorbent having an average pore size of 3.5 to 6 Å, to reduce the content of the compound. The purified gas can be used as a low temperature refrigerant or an etching gas.

(HFC).

In order to obtain high-purity pentafluoroethane, these impurities must be removed as much as possible. Among these impurities, various purification methods have been proposed to remove chlorofluorocarbons not only for attaining high purity but also for preventing the depletion of the ozone layer. Chloropentafluoroethane is a compound having a boiling point close to that of pentafluoroethane and difficult to separate by ordinary distillation, however, for example, the following purification methods may be used therefor:

(1) a method by extractive distillation (see, Japanese International Application Domestic Publication No. 9-508626 (JP-A-9-508626)),

(2) a method of reducing and hydrogenating chloropentafluoroethane (see, Japanese Unexamined Patent Publication No. 8-301801 (JP-A-8-301801)),

(3) a method of removing chloropentafluoroethane after fluorinating it with hydrogen fluoride (HF) (see, Japanese Unexamined Patent Publication No. 2001-48816 (JP-A-2001-48816)), and

(4) a method of removing chloropentafluoroethane after adsorbing it by using an adsorbent (see, Japanese Unexamined Patent Publication No. 6-92879 (JP-A-6-92879)).

Chloromethane (CH_3Cl), which is one of hydrochlorocarbons, forms an azeotropic mixture or azeotrope-like mixture with pentafluoroethane and this compound is very difficult to separate from the pentafluoroethane. Furthermore, difluoromethane (CH_2F_2) and 1,1,1-trifluoroethane (CF_3CH_3), which are hydrofluorocarbons, each form an azeotropic mixture or azeotrope-like mixture with pentafluoroethane and these compounds are very difficult to separate from the pentafluoroethane.

As for the method of purifying and thereby removing impurities comprising these difficult-to-separate

comprising bringing crude pentafluoroethane containing at least one compound selected from the group consisting of hydrofluorocarbons containing one carbon atom, hydrochlorofluorocarbons containing one carbon atom and hydrochlorocarbons containing one carbon atom, into contact with an adsorbent comprising a zeolite having an average pore size of 3 to 6 Å and a silica/aluminum ratio of 2.0 or less and/or a carbonaceous adsorbent having an average pore size of 3.5 to 6 Å, to reduce the content of the compound contained as an impurity in the crude pentafluoroethane.

[2] The process as described in [1] above, wherein the hydrofluorocarbon containing one carbon atom is selected from the group consisting of fluoromethane, difluoromethane and trifluoromethane.

[3] The process as described in [1] above, wherein the hydrochlorofluorocarbon containing one carbon atom is chlorodifluoromethane.

[4] The process as described in [1] above, wherein the hydrochlorocarbon containing one carbon atom is selected from the group consisting of chloromethane, dichloromethane and trichloromethane.

[5] The process as described in any one of [1] to [4] above, wherein the total content of the compound contained as an impurity in the crude pentafluoroethane is 1 vol% or less.

[6] The process as described in any one of [1] to [5] above, wherein the crude pentafluoroethane is brought into contact with the adsorbent under a pressure of 1 MPa or less.

[7] The process as described in any one of [1] to [6] above, wherein the total content of the compound contained as an impurity in the crude pentafluoroethane is reduced to 150 vol ppm or less.

[8] The process as described in any one of [1] to [7] above, wherein the total content of hydrofluorocarbons containing one carbon atom, contained

as an impurity in the crude pentafluoroethane, is reduced to 100 vol ppm or less.

[9] The process as described in any one of [1] to [8] above, wherein the total content of hydrochlorocarbons containing one carbon atom, contained as an impurity in the crude pentafluoroethane, is reduced to 50 vol ppm or less.

[10] The process as described in any one of [1] to [9] above, wherein the crude pentafluoroethane is obtained by a process comprising the following steps:

(1) a step of reacting at least one member selected from the group consisting of tetrachloroethylene, 2,2-dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain pentafluoroethane, and

(2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound, or a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound.

[11] A process for producing pentafluoroethane, comprising the following steps:

(1) a step of reacting at least one member selected from the group consisting of tetrachloroethylene, 2,2-dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain pentafluoroethane,

(2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound, or a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound, and

(3) a step of purifying the pentafluoroethane obtained in step (2) by using the process described in any one of [1] to [10] above.

5 [12] A process for producing hexafluoroethane, comprising reacting a fluorine gas with pentafluoroethane purified by using the process described in any one of [1] to [10] above.

10 [13] A refrigerant comprising pentafluoroethane purified by using the process described in any one of [1] to [10] above.

Best Mode for Carrying Out the Invention

The preferred embodiments of the present invention are described below.

15 As described above, for the production of a pentafluoroethane, for example, a method of fluorinating tetrachloroethylene or a fluoride thereof with hydrogen fluoride (HF) in the presence of a fluorination catalyst is known.

20 When pentafluoroethane is produced by this method, even if a generally employed purification step such as distillation is performed, impurities which are difficult to separate from pentafluoroethane are contained in the material. Examples of the impurity include hydrofluorocarbons, hydrochlorofluorocarbons and 25 hydrochlorocarbons. Also, even if a method of hydrogen-reducing chloropentafluoroethane in the presence of a catalyst is used, these impurities are similarly contained. Accordingly, in order to purify pentafluoroethane to a high purity, these impurities must 30 be removed.

35 The process for purifying pentafluoroethane of the present invention is characterized in that crude pentafluoroethane containing at least one compound selected from the group consisting of hydrofluorocarbons containing one carbon atom, hydrochlorofluorocarbons containing one carbon atom and hydrochlorocarbons containing one carbon atom is brought into contact with

dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain pentafluoroethane, and

5 (2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound, or a step of bringing pentafluoroethane obtained in step
10 (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound.

Step (1) may use a method of performing a fluorination reaction between the starting material, for example, tetrachloroethylene, and hydrogen fluoride
15 through two stages in the presence of a fluorination catalyst to obtain pentafluoroethane. The fluorination catalyst is preferably a supported or bulk catalyst mainly comprising a trivalent chromium oxide.

In step (2), in the case of performing the step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, this may be performed in the presence of a supported catalyst where at least one member selected from the group consisting of palladium,
20 rhodium, ruthenium, rhenium, platinum and gold is supported on a support. The reaction temperature is from 150 to 400°C. By the contact with hydrogen, a reduction and hydrogenation reaction of, for example, hydrochlorocarbons takes place.

In step (2), in the case of performing the step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound, this may be performed in the presence of a supported or bulk catalyst mainly comprising a trivalent chromium oxide or in the presence of a supported catalyst where at least one member selected from the group consisting of palladium, rhodium, ruthenium, rhenium, platinum and gold is supported on a support. The reaction temperature is
35

from 150 to 400°C. Examples of the oxygen-containing compound which can be used include nitrogen monoxide (NO), nitrous oxide (N₂O), nitrogen dioxide (NO₂) and ozone (O₃). By this treatment, hydrofluorocarbons contained as an impurity can be converted into CO₂ or the like. Step (2) is preferably performed by bringing the pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound.

After the compound contained as an impurity in the crude pentafluoroethane is treated with the adsorbent, the total content of the compound contained in the pentafluoroethane can be reduced to 150 vol ppm or less, even to 100 vol ppm or less. Also, the total content of the hydrofluorocarbons containing one carbon atom, contained as an impurity in pentafluoroethane purified by using the purification process of the present invention, can be reduced to 100 vol ppm or less, even to 50 vol ppm or less. Furthermore, the total content of the hydrochlorocarbons containing one carbon atom can be reduced to 50 vol ppm or less, even to 30 vol ppm or less. The content of the compound contained as an impurity in pentafluoroethane can be measured by gas chromatography (GC) using TCD method or FID method, or gas chromatography-mass spectrometry (GC-MS).

The present invention also provides a process for producing pentafluoroethane, comprising the following steps:

(1) a step of reacting at least one member selected from the group consisting of tetrachloroethylene, 2,2-dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain a pentafluoroethane,

(2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound,

or a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound, and

5 (3) a step of purifying pentafluoroethane obtained in step (2) by using the process described above.

Uses of pentafluoroethane obtained by using the purification process of the present invention are described below.

10 The high-purity pentafluoroethane is a substitute for chlorodifluoromethane (CHClF_2) which is currently used as a working fluid of cryogenic refrigerators, and this can be used as a mixed refrigerant comprising difluoromethane/pentafluoroethane/1,1,1,2-tetrafluoroethane and also as a mixed refrigerant comprising difluoromethane/pentafluoroethane.

15 Furthermore, the high-purity pentafluoroethane can be used as a starting material for the production of hexafluoroethane. Particularly, in the method of producing hexafluoroethane by a reaction of pentafluoroethane with a fluorine gas, when the high-purity pentafluoroethane is used as a starting material, the production of impurities which are difficult to separate from the objective hexafluoroethane can be prevented. In addition, when the high-purity pentafluoroethane is used as a starting material, the latitude in setting the fluorination reaction conditions can be broadened and, as a result, the reaction can be stably controlled and the purification step can be simplified.

20 The high-purity pentafluoroethane or a mixed gas thereof with an inert gas (e.g., He, N₂, Ar), HCl, O₂, H₂ or the like can be used as an etching gas in the etching step in the process of producing a semiconductor device. In the process of producing a semiconductor device such as an LSI, a TFT and an organic EL, a thin or thick film is formed using a CVD method, a sputtering method or a vapor deposition method and a circuit pattern is formed

by etching, where a gas containing the pentafluoroethane can be used as the etching gas. The etching using pentafluoroethane can be performed under various dry etching conditions such as plasma etching and microwave etching.

The present invention is further illustrated below by referring to the following examples, however, the present invention is not limited to these examples.

Preparation Example 1 of Crude Pentafluoroethane
10 (Raw Material Example 1)

Tetrachloroethylene and hydrogen fluoride were introduced into a first reactor filled with a catalyst to produce a gas mainly comprising 2,2-dichloro-1,1,1-trifluoroethane and chloro-1,1,1,2-tetrafluoroethane which are intermediates. This gas was introduced together with HF into a second reactor to produce pentafluoroethane. The produced pentafluoroethane was distilled to obtain pentafluoroethane containing, as impurities, chloropentafluoroethane, fluoromethane, difluoromethane, chloromethane, chlorodifluoromethane, 1,1,1-trifluoromethane and the like. The purity of the pentafluoroethane was about 99.4 vol%. Subsequently, this pentafluoroethane was reacted with hydrogen in the presence of a commercially available hydrogenation catalyst (reaction pressure: 0.15 MPa, reaction temperature: 220°C). The acid content contained in the product mainly comprising pentafluoroethane was removed by a known method and the residue was distilled to obtain a crude pentafluoroethane. The obtained crude pentafluoroethane was analyzed by a gas chromatograph and found to have the composition shown in Table 1.

Table 1

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.8404
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0024
CF ₃ CH ₃	0.0879
CH ₂ F ₂	0.0482
CHF ₃	0.0021
CHClF ₂	0.0020
CH ₃ Cl	0.0088

Preparation Example 2 of Crude Pentafluoroethane
(Raw Material Example 2)

The pentafluoroethane obtained in Raw Material

5 Example 1 was introduced together with air into a reactor filled with a palladium/aluminum catalyst and reacted under such conditions that the reaction pressure was 0.2 MPa and the reaction temperature was 280°C. The acid content and carbon dioxide contained in the gas at the

10 outlet of the reactor were partially removed by washing the gas with an aqueous potassium hydroxide solution and then the gas was distilled to obtain a crude pentafluoroethane. The obtained crude pentafluoroethane was analyzed by a gas chromatograph and found to have the

15 composition shown in Table 2.

Table 2

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.9522
CF ₃ CClF ₂	0.0081
CF ₃ CH ₂ F	0.0018
CF ₃ CH ₃	0.0088
CH ₂ F ₂	0.0246
CHF ₃	0.0019
CHClF ₂	0.0020
CH ₃ Cl	0.0087

Preparation Example 3 of Crude Pentafluoroethane
(Raw Material Example 3)

To the crude pentafluoroethane obtained in Raw

20 Material Example 2, CH₂F₂ and CH₃Cl were further added to prepare a crude pentafluoroethane raw material 3. This was analyzed by a gas chromatograph and found to have the composition shown in Table 3.

Table 3

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.6322
CF ₃ CCLF ₂	0.0081
CF ₃ CH ₂ F	0.0018
CF ₃ CH ₃	0.0087
CH ₂ F ₂	0.2325
CHF ₃	0.0019
CHClF ₂	0.0020
CH ₃ Cl	0.1128

Example 1

5 A zeolite (Molecular Sieves 4A (produced by Union Showa K.K., average pore size: 3.5 Å, silica/aluminum ratio = 1.0)) (20 g) was filled in a 200 ml stainless steel cylinder and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 1 was filled while cooling the cylinder and occasionally stirred while keeping the temperature at -10°C. After 10 about 20 hours, the liquid phase part was analyzed by a gas chromatograph. The analysis results are shown in Table 4.

Table 4

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.8979
CF ₃ CCLF ₂	0.0082
CF ₃ CH ₂ F	0.0021
CF ₃ CH ₃	0.0880
CH ₂ F ₂	0.0001
CHF ₃	0.0015
CHClF ₂	0.0019
CH ₃ Cl	0.0003

15 As apparent from the analysis results shown in Table 4, CH₂F₂ and CH₃Cl could be selectively adsorbed and removed.

Example 2

20 Molecular Sieves 4A (20 g) was filled into a 200 ml stainless steel cylinder in the same manner as in Example 1 and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 2 was filled while cooling the cylinder and occasionally stirred while keeping the temperature at room temperature (20°C). After about 20 hours, the liquid phase part was analyzed

by a gas chromatograph. The analysis results are shown in Table 5.

Table 5

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.9790
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0017
CF ₃ CH ₃	0.0087
CH ₂ F ₂	0.0001
CHF ₃	0.0009
CHClF ₂	0.0012
CH ₃ Cl	0.0002

As apparent from the analysis results shown in Table 5, a high-purity pentafluoroethane having a purity of 99.97 vol% or more was obtained.

Example 3

Molecular Sieves 4A (30 g) was filled into a 200 ml stainless steel cylinder in the same manner as in Example 1. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 3 was filled while cooling the cylinder, vacuum-dried and then occasionally stirred while keeping the temperature at room temperature (25°C). After about 20 hours, the liquid phase part was analyzed by a gas chromatograph. The analysis results are shown in Table 6.

Table 6

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.9789
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0016
CF ₃ CH ₃	0.0087
CH ₂ F ₂	0.0011
CHF ₃	0.0006
CHClF ₂	0.0008
CH ₃ Cl	0.0001

Example 4

A carbonaceous adsorbent (Molecular Sieving Carbon, produced by Takeda Chemical Industries, Ltd., average pore size: 4 Å) (20 g) was filled into a 200 ml stainless steel cylinder and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 1 was filled while cooling the cylinder and occasionally

stirred while keeping the temperature at -20°C. After about 20 hours, the liquid phase part was analyzed by a gas chromatograph. The analysis results are shown in Table 7.

5

Table 7

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.8992
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0023
CF ₃ CH ₃	0.0880
CH ₂ F ₂	0.0003
CHF ₃	0.0006
CHClF ₂	0.0012
CH ₃ Cl	0.0002

As apparent from the analysis results shown in Table 7, CH₂F₂ and CH₃Cl could be selectively adsorbed and removed.

Example 5

10

Molecular Sieves 4A (15 g) used in Example 1 and 15 g of Molecular Sieving Carbon used in Example 4 were mixed and filled into a 200 ml stainless steel cylinder and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 3 was filled while cooling the cylinder and occasionally stirred while keeping the temperature at room temperature (25°C). After about 20 hours, the liquid phase part was analyzed by a gas chromatograph. The analysis results are shown in Table 8.

15

Table 8

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.9786
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0017
CF ₃ CH ₃	0.0088
CH ₂ F ₂	0.0004
CHF ₃	0.0007
CHClF ₂	0.0013
CH ₃ Cl	0.0003

Comparative Example 1

A zeolite (Molecular Sieves 13X (produced by Union Showa K.K., average pore size: 10 Å, silica/aluminum ratio = 1.2)) (20 g) was filled in a 200 ml stainless

steel cylinder and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 2 was filled while cooling the cylinder and occasionally stirred while keeping the temperature at room temperature (25°C). After about 20 hours, the liquid phase part was analyzed by a gas chromatograph. The analysis results are shown in Table 9.

Table 9

Compound	Concentration (vol%)
CF ₃ CHF ₂	99.9452
CF ₃ CClF ₂	0.0082
CF ₃ CH ₂ F	0.0002
CF ₃ CH ₃	0.0090
CH ₂ F ₂	0.0251
CHF ₃	0.0012
CHClF ₂	0.0021
CH ₃ Cl	0.0090

As apparent from the analysis results shown in Table 9, even when the silica/aluminum ratio is 2.0 or less, if the average pore size exceeds 6 Å, the selective adsorption and removal cannot be attained.

Comparative Example 2

An activated carbon (granular Shirosagi KL (produced by Takeda Chemical Industries, Ltd., average pore size: 35 Å)) (20 g) was filled in a 200 ml stainless steel cylinder and vacuum dried. Thereto, about 100 g of the crude pentafluoroethane of Raw Material Example 2 was filled while cooling the cylinder and occasionally stirred while keeping the temperature at room temperature (25°C). After about 20 hours, the liquid phase part was analyzed by a gas chromatograph. Similarly to Comparative Example 1, the selective adsorption and removal could not be attained and the reduction in the content of CH₂F₂ or CH₃Cl was not attained.

Comparative Example 3

The purification was performed by the same operation under the same conditions as in Comparative Example 1 except for filling a zeolite (H-ZSM-5 (produced by N.E. Chemcat Corporation, average pore size: 6 Å,

silica/aluminum ratio = 15)) into the 200 ml stainless steel cylinder. As a result of analysis, the reduction in the content of CH₂F₂ or CH₃Cl was not confirmed.

Industrial Applicability

As described in the foregoing pages, when the purification process of the present invention is used, high-purity pentafluoroethane can be obtained. Pentafluoroethane obtained according to the present invention can be used as a low temperature refrigerant or a starting material for the production of high-purity hexafluoroethane.

CLAIMS

1. A process for purifying pentafluoroethane, comprising bringing crude pentafluoroethane containing at least one compound selected from the group consisting of hydrofluorocarbons containing one carbon atom, hydrochlorofluorocarbons containing one carbon atom and hydrochlorocarbons containing one carbon atom, into contact with an adsorbent comprising a zeolite having an average pore size of 3 to 6 Å and a silica/aluminum ratio of 2.0 or less and/or a carbonaceous adsorbent having an average pore size of 3.5 to 6 Å, to reduce the content of said compound contained as an impurity in the crude pentafluoroethane.

2. The process as claimed in claim 1, wherein said hydrofluorocarbon containing one carbon atom is selected from the group consisting of fluoromethane, difluoromethane and trifluoromethane.

3. The process as claimed in claim 1, wherein said hydrochlorofluorocarbon containing one carbon atom is chlorodifluoromethane.

4. The process as claimed in claim 1, wherein said hydrochlorocarbon containing one carbon atom is selected from the group consisting of chloromethane, dichloromethane and trichloromethane.

5. The process as claimed in any one of claims 1 to 4, wherein the total content of said compound contained as an impurity in the crude pentafluoroethane is 1 vol% or less.

6. The process as claimed in any one of claims 1 to 5, wherein the crude pentafluoroethane is brought into contact with said adsorbent under a pressure of 1 MPa or less.

7. The process as claimed in any one of claims 1 to 6, wherein the total content of said compound contained as an impurity in the crude pentafluoroethane is reduced to 150 vol ppm or less.

8. The process as claimed in any one of claims 1

to 7, wherein the total content of hydrofluorocarbons containing one carbon atom, contained as an impurity in the crude pentafluoroethane, is reduced to 100 vol ppm or less.

5 9. The process as claimed in any one of claims 1 to 8, wherein the total content of hydrochlorocarbons containing one carbon atom, contained as an impurity in the crude pentafluoroethane, is reduced to 50 vol ppm or less.

10 10. The process as claimed in any one of claims 1 to 9, wherein the crude pentafluoroethane is obtained by a process comprising the following steps:

15 (1) a step of reacting at least one member selected from the group consisting of tetrachloroethylene, 2,2-dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain pentafluoroethane, and

20 (2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound, or a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound.

25 11. A process for producing pentafluoroethane, comprising the following steps:

30 (1) a step of reacting at least one member selected from the group consisting of tetrachloroethylene, 2,2-dichloro-1,1,1-trifluoroethane and 2-chloro-1,1,1,2-tetrafluoroethane with hydrogen fluoride in the presence of a fluorination catalyst to obtain pentafluoroethane,

35 (2) a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen, a step of bringing pentafluoroethane obtained in step (1) into contact with oxygen and/or an oxygen-containing compound,

or a step of bringing pentafluoroethane obtained in step (1) into contact with hydrogen and then into contact with oxygen and/or an oxygen-containing compound, and

5 (3) a step of purifying pentafluoroethane obtained in step (2) by using the process claimed in any one of claims 1 to 10.

12. A process for producing hexafluoroethane, comprising reacting a fluorine gas with pentafluoroethane purified by using the process claimed in any one of

10 claims 1 to 10.

13. A refrigerant comprising pentafluoroethane purified by using the process claimed in any one of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 03/08295

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C17/389 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 22793 A (DU PONT ;CORBIN DAVID R (US); DIEBOLD MICHAEL PATRICK (US); MAHLER) 13 October 1994 (1994-10-13) claims 1,5,9; example 1; table 1 ---	1-11
X	US 5 453 551 A (LACROIX ERIC ET AL) 26 September 1995 (1995-09-26) column 5, example 1B; column 1, line 20 - line 23 ---	12,13
Y	WO 01 83412 A (OHNO HIROMOTO ;OHI TOSHI (JP); SHOWA DENKO KK (JP)) 8 November 2001 (2001-11-08) page 6, line 36 - page 7, line 7; page 7, line 8 - page 8, line 7; page 14, lines 1-5; claims 1-4; example 1; table 4 ---	1-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International	Application No
PCT/JP	03/08295

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9422793	A	13-10-1994	WO	9422793 A1		13-10-1994
			AU	3974293 A		24-10-1994
			EP	0693047 A1		24-01-1996
			JP	8508479 T		10-09-1996
			US	5585529 A		17-12-1996
US 5453551	A	26-09-1995	FR	2701943 A1		02-09-1994
			AU	652321 B1		18-08-1994
			CA	2115975 A1		25-08-1994
			CN	1099022 A		22-02-1995
			DE	69400036 D1		18-01-1996
			DE	69400036 T2		18-07-1996
			EP	0612709 A1		31-08-1994
			ES	2081226 T3		16-02-1996
			JP	6256234 A		13-09-1994
WO 0183412	A	08-11-2001	JP	2001302566 A		31-10-2001
			AU	5261701 A		12-11-2001
			WO	0183412 A2		08-11-2001
			US	2003034309 A1		20-02-2003